Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

The most practical remedy for the apple scab must be one that may be applied in the same water with Paris green or London purple without thereby endangering the foliage. It is the opinion of our station chemist, Dr. Babcock, that not only the ammoniacal copper carbonate, but the sodium hyposulphite and the sulphides of lime and potash, all tend to render the arsenic of Paris green and London purple soluble, and hence can not be wisely used in connection with these poisons. The copper carbonate, however, which in the ammoniacal solution is the beneficial agent in preventing the apple scab, does not have this effect when used without the ammonia. The question therefore arises, is the ammonia solvent necessary?

I have recently made some tests with a sample of commercial precipitated copper carbonate, and find that its state of division is such that it remains suspended in water rather better than Paris green, and so may be applied by any apparatus that successfully distributes the latter. It apparently adheres to the foliage nearly or quite as well, when applied in simple suspension, as in the diluted ammoniacal solution.

I recommend, therefore, that those who spray their apple trees for the prevention of injury from the codling moth, make the experiment in a portion of the orchard of adding the precipitated copper carbonate to the water, at the rate of an ounce to twenty-five gallons. No harm to the foliage can result from this measure, while we have every reason to expect that much benefit will accrue in the prevention of the apple scab.

UNIVERSITY OF WISCONSIN, MADISON, WIS.

THE COPPER SALTS AS FUNGICIDES.

BY F. D. CHESTER.

In order to make an intelligent comparison between the several well known fungicides containing copper, it is important to understand what salts of copper occur in each and in what relative proportions. This in turn involves some inquiry into the chemical reactions which take place in their preparation and during their stay upon the vine.

For much valuable assistance in the preparation of these notes I am indebted to Prof. C. L. Penny, the Chemist of this Station.

THE BORDEAUX MIXTURE.

Formula.—Copper sulphate, 6 pounds; lime, 6 pounds; water, 22 gallons. In the addition of milk of lime to a solution of copper sulphate, the lime in solution precipitates the copper as cupric hydroxide, forming at the same time a slightly soluuble sulphate of lime. These two salts, together with an excess of lime, remain in suspension in the Bordeaux mixture.

The reaction is simple:

$$CuSO_4, 5H_2O + CaO,H_2O = Cu\ (OH)_2 + CaSO_4 + 5H_2O.$$

From this formula a simple calculation shows that to precipitate the 6 pounds of copper sulphate, there would be required 1.34 pounds of lime (CaO), which would in turn produce 2.34 pounds of cupric hydroxide.

The weight of lime to be used should be considerably increased above this amount, owing to its impure character as ordinarily purchased, but it is likely that 3 or 4 pounds of commercial lime will suffice to satisfy this reaction.

The 22 gallons of water is capable of dissolving approximately .235 pounds of lime, an amount sufficient to precipitate practically 1 pound of the copper sulphate. But since this quantity of lime is immediately thrown down as a nearly insoluble sulphate, the water is free to dissolve another portion of lime, which in turn precipitates another portion of the copper, until all of the copper is thrown down. It is found that this complete precipitation of the copper takes place quickly, or by the time the matter in suspension has fully settled, leaving a clear supernatant liquid, which does not react for copper; hence a long standing of the Bordeaux mixture before use is hardly necessary.

In drying upon the plant the cupric hydroxide in the Bordeaux mixture undergoes no change, hence it is probably this salt of copper which is the active principle.

EAU CELESTE.

Formula.—Copper sulphate, 1 pound; strong ammonia, 1½ pints; water, 22 gallons.

In the addition of ammonia water to a solution of normal copper sulphate, the copper is precipitated as a basic sulphate, forming at the same time ammonic sulphate, which remains in solution. With an excess of ammonia, the basic copper sulphate dissolves to a blue fluid forming the ammonio-copper sulphate ($CuSO_4, 4NH_3, H_2O$).

In drying upon the plant the ammonio-copper sulphate gradually loses its ammonia and is reconverted into the basic copper sulphate. The following are the probable reactions:

(1) $$\underset{\substack{\text{Normal cop-}\\ \text{per sulphate}}}{\underline{3CuSO_4, 5H_2O}} + 4NH_4HO = \underset{\substack{\text{Basic copper}\\ \text{sulphate.}}}{\underline{CuSO_4\,2Cu(OH)_2}} + 2(NH_4)_2\ SO_4 + 15H_2O$$

(2) $$CuSO_4, 2Cu(OH)_2 + 2(NH_4)_2SO_4 + \underset{\text{In excess.}}{\underline{8NH_4HO}} = \underset{\substack{\text{Ammonium copper}\\ \text{sulphate.}}}{\underline{3(CuSO_4, 4NH_3, H_2O)}} + 9H_2O$$

(3) In drying upon the vine.
$$3(CuSO_4, 4NH_3, H_2O) + H_2O = CuSO_4, 2Cu(OH)_2 + 2(NH_4)_2SO_4 + 8NH_3$$

To satisfy the reactions (1) and (2), the one pound of copper sulphate would require .439 pounds of ammonia gas (NH_3); or 1.66 pints of the stronger water of ammonia of the U. S. Pharmacopœia (sp. gr. 0.900 at 15° C.), producing in turn .47 pounds of the basic copper sulphate.

MODIFIED EAU CELESTE.

Formula.—Sulphate of copper, 2 pounds; carbonate of soda, 2½ pounds; strong ammonia, 1½ pints; water, 22 gallons. In the addition of a solution of sodic carbonate to a solution of copper carbonate the copper is precipitated as a basic carbonate, forming at the same time a soluble sulphate of soda.

Upon the addition of ammonia the basic carbonate dissolves to a blue fluid forming the ammonio-copper carbonate ($CuCO_3, 2NH_3$), and the ammonio-cupric hydroxide. ($3Cu(OH)_2, 4NH_3, 3H_2O$.)

In drying upon the plant both of these salts gradually lose their ammonia, and are converted into the basic carbonate and into the cupric hydroxide.

The following are the probable reactions:

(1)

$$12(CuSO_4,\ 5H^2O) + 12(Na_2CO_3,\ 10H_2O) = 6\underbrace{[CuCO_3,\ Cu(OH)_2,}_{\text{Basic carbonate of copper.}}\ H_2O] +$$

$$12Na_2SO_4 + 6CO_2 + 168H_2O$$

(2)

$$6[CuCO_3,\ CuC(OH)_2] + \underbrace{20NH_4HO}_{\text{To dissolve.}} = \underbrace{6(CuCO_3,\ 2NH_3)}_{\text{Ammonio-copper carbonate.}} +$$

$$2\underbrace{[3Cu(OH)_2,\ 4NH_3,\ 3H_2O]}_{\text{Ammonio-cupric hydroxide.}} + 14H_2O.$$

(3) In drying upon the plant.

$$6(CuCO_3,\ 2NH_3) + 6H_2O = 3\underbrace{[CuCO_3,\ Cu(OH)_2]}_{\text{Basic carbonate of copper.}} + 3(NH_4)_2CO_3 + 6NH_3$$

$$2[3Cu(OH)_2,\ 4NH_3,\ 3H_2O] = 6Cu(OH)_2 + 8NH_3 + 6H_2O.$$

From the above formula it is found that to satisfy the reaction, the two pounds of copper sulphate will require 2.3 pounds of crystallized carbonate of soda, which will eventually produce .44 pounds of basic carbonate of copper and .38 pounds of the cupric hydroxide, or a total of .82 pounds of the mixed salts.

AMMONIACAL COPPER CARBONATE.

Formula.—Copper carbonate, 3 ounces; strong ammonia, 1 quart; water, 22 gallons.

In the preparation of this solution, the chemistry is the same as that given under modified eau celeste and the reactions are given in formulæ (2) and (3).

Upon the same basis as before, 3 ounces of copper carbonate will yield 1.5 ounces of basic carbonate and 1.32 ounces of cupric hydroxide, or a total of 2.82 ounces. The difference between the modified eau celeste and the ammoniated copper carbonate consists in the presence of sodium sulphate in the former material, and its absence in the latter. Whether this sodium sulphate will be at all harmful to foliage is a question to be decided by experiment, and the writer would advise that this question be tested. The cost of the copper carbonate in the modified eau celeste is approximately 20 cents per pound, while the cost of the commercial carbonate, is, according to present quotations, 65 cents per pound. Furthermore it is seen from the following table that the cost of the basic salts of copper deposited upon the plant, is, in the modified eau celeste, 29 cents per pound, and in the ammoniacal copper carbonate 94 cents per pound; a difference worthy of serious consideration.

In the use of both the modified eau celeste and the ammoniacal copper carbonate there is not produced continually a basic carbonate of copper, but a mixture of the basic carbonate, and the hydroxide. Would it not therefore be well to try the pure basic carbonate either by precipitating the copper with sodium carbonate, and applying it in suspension as the hydroxide is applied in the Bordeaux mixture or by dissolving this precipitate in ammonium carbonate? By the former method, using 2 pounds of copper sulphate, and 2¼ pounds of sodium carbonate, we would have an extremely cheap and perhaps effective fungicide.

The following table has been constructed that the facts contained in this paper might be presented in a condensed form.

The writer in conclusion would particularly recommend that the relative value of the hydroxide, the basic sulphate, and the basic carbonate be tested by the application of materials containing equal weights of these salts per unit of water.

Name of fungicide.	Form of salts when dry upon the plant.	Weight of foregoing salts per 22 gallons.	Weight of original copper salt to make 1 pound of salt when dry on plant.	*Cost of fungicides per 22 gallons.	Cost of 1 pound of copper salt when dry on plant.
		Pounds.	*Pounds.*	*Cents.*	
Bordeaux mixture	Cupric hydroxide, $Cu(OH)_2$	2.34	2.5	34.25	$0.146
Eau celeste	Basic copper sulphate, $Cu SO_4$, $2Cu(OH)_2$.	.47	2.13	21.25	.452
Modified eau celeste	Basic copper carbonate, $Cu CO_3$, $Cu(OH)_2$, and Cupric hydroxide, $Cu(OH)_2$.	.82	2.44	24.37	.297
Ammoniacal copper carbonate.	Basic copper carbonate, $Cu CO_3$, $Cu(OH)_2$, and Cupric hydroxide, $Cu(OH)_2$.	*Ounces.* 2.82	1.06	16.6	.942

Delaware College, Newark, Del.

---

* Wholesale cost of materials from which calculations in the last two columns of the above table were made: Copper sulphate, 5⅜ cents per pound; sal soda, 1¼ cents per pound; strong ammonia (26°), 7 cents per pound; copper carbonate precipitated from copper sulphate by sal soda, 13.87 cents per pound.